PATENT SPECIFICATION

NO DRAWINGS

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International Classification:—C09b.

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are DIETER LEUCHS and HANS BAUMANN, citizens of Germany and residents, respectively, of 174 Mundenheimerstrasse, Ludwigshafen/Rhein, Germany; and 8 Alwin-Mittasch-Platz, Ludwigshafen/Rhein, Germany.

COMPLETE SPECIFICATION

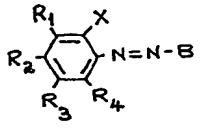
New Chromium and Cobalt Complex Monoazo Dyestuffs, their production and use

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of Ludwigshafen/Rhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new chromium and cobalt complex dyestuffs, a process for their production, and their use for dyeing wool and synthetic textile materials.

It is an object of this invention to provide new chromium and cobalt complexes which will dye wool, synthetic linear polyamides, synthetic linear polyesters and mixtures of wool and synthetic linear polyamides or synthetic linear polyesters in vivid shades of excellent fastness properties.

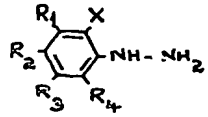
Another object of the invention is to provide a process for the production of the said chromium and cobalt complexes. We have found that the said chromium and cobalt complex dyestuffs are obtained by treating with an agent which supplies chromium or cobalt an azo dyestuff of the general formula I



I

in which X represents a hydroxy group, a methoxy group or a carboxy group, R_1 represents a hydrogen atom, a chlorine atom or a nitro group, R_2 represents a hydrogen atom, a nitro group, a methylsulphone group, an ethylsulphone group or a sulphonic acid amide group, R_3 represents a hydrogen atom, a chlorine atom, a methyl group, a methoxy group, a nitro group, a methylsulphone group, an ethylsulphone group, a sulphonic acid amide group or a sulphonic acid methylamide group, R_4 represents a hydrogen atom or a chlorine atom, and B represents a 2-hydroxyindolyl-3, a 1 - methyl - 2 - hydroxy - indolyl - 3, a 2 - hydroxy - 5 - chlorindolyl-3, a 2 - hydroxy - 5,7 - dichlorindolyl-3, a 2 - hydroxy - 5 - nitroindolyl - 3, a 2-hydroxy - thionaphthyl - 3, a 2 - hydroxy-5 - methylthionaphthyl - 3, a 2 - hydroxyacenaphthyl - 1 or a 9 - hydroxyphenanthryl-10 radical.

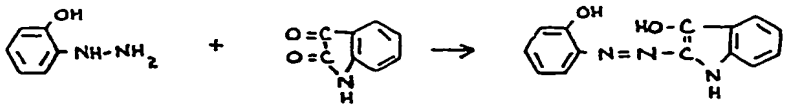
Azo dyestuffs of the general formula I may be obtained by reacting a phenyl hydrazine of the general formula II:



II

in which X, R_1, R_2, R_3 and R_4 have the above meanings with a dioxo compound such as isatin, 1-methylisatin, 5-chlorisatin, 5,7-dichlorisatin, 5 - nitroisatin, thionaphthenequinone - (1,2), 5 - methylthionaphthenequinone - 2,3), phenanthrene - quinone - (9,10) or acenaphthene-quinone-(1,2).

The reaction of the phenyl hydrazines of the formula II with the said dioxo compounds is carried out in strong acid medium, for example in strong aqueous hydrochloric acid medium. The course of the reaction is shown by the following scheme in which the reaction of 2-hydroxyphenylhydrazine with isatin is reproduced by way of example:



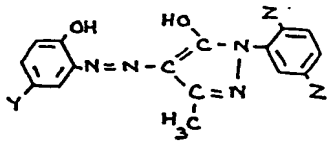
Some of the phenyl hydrazines of the formula II in which X represents a methoxy or a carboxy group are known from the literature. These phenyl hydrazines may be prepared in the usual way for example by reduction of the corresponding diazo compounds. Ortho-hydroxyphenyl hydrazines free from sulphonic acid groups have however not hitherto been described; they are very decomposable and may therefore only be isolated with difficulty. We have found however that for the reaction with the said dioxo compounds, the isolation of the ortho-hydroxyphenyl hydrazines is not necessary. Rather there may be used for the production of the new azo dyestuffs of the formula I, the solutions obtained by reduction of the corresponding ortho-hydroxydiazo compounds in aqueous medium, without the ortho-hydroxyphenyl hydrazines being recovered in pure form. The best results are achieved by reducing the ortho-hydroxybenzene diazonium salts with tin (II) chloride in aqueous hydrochloric acid medium or reducing the ortho-hydroxybenzene diazosulphonates with zinc dust in aqueous acetic acid medium or with sodium dithionite in aqueous medium. The solutions of ortho-hydroxyphenyl hydrazine sulphonates thus obtained can be directly used for reaction with the above-mentioned dioxo compounds.

The same method of operation is also especially suitable for the production and further reaction of the ortho-methoxyphenyl or ortho-carboxyphenyl hydrazines to the dyestuffs of this invention.

For conversion into the chromium or cobalt complexes the azo dyestuffs of the formula I are treated in aqueous solution or aqueous suspension or in organic solvents at room temperature or at elevated temperature with agents supplying chromium or cobalt. Examples of agents supplying cobalt are the water-soluble salts of divalent cobalt, such as cobalt sulphate, cobalt chloride, cobalt acetate, cobalt nitrate or cobalt formate. Examples of agents supplying chromium are chromium (III) oxide or the water-soluble salts of trivalent chromium, such as chromium chloride, chromium sulphate, chromium formate or chromium acetate. As organic solvents for the chroming or cobalting there may be used especially well those which are miscible with water, such as formamide, dimethylformamide or di - (2 - hydroxyethyl) ether.

By the said chroming or cobalting there are obtained chromium or cobalt complexes which contain one to two radicals of an azo dyestuff of the formula I attached to one chromium or cobalt atom.

When the chromium or cobalt complex dyestuffs just described contain less than two dyestuff radicals attached to one chromium or cobalt atom, they may be reacted with another dyestuff of the formula I or with a dyestuff of the formula III



III

in which Y represents a sulphonic acid amide or nitro group and Z represents a hydrogen atom or a chlorine atom, to form a chromium or cobalt complex dyestuff which contains, attached to a chromium or cobalt atom, two different radicals of dyestuffs of the formula I or one radical of a dyestuff of the formula I and one dyestuff of the formula III.

This reaction is preferably carried out in aqueous solution at elevated temperature, for example 70° to 100° C. and with the addition of basic substances, as for example sodium hydroxide.

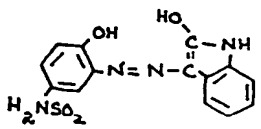
The new chromium and cobalt complex dyestuffs are easily soluble in organic solvents. They are especially suitable for dyeing wool, from a neutral to weak acid bath, linear fibre-forming polyamides, such as nylon and polycaprolactam, linear fibre-forming polyesters, such as polyethyleneterephthalate and polyhexahydroterephthalyl terephthalate, and mixtures of the wool and the said polyamides or polyesters.

The following Examples will further illustrate this invention in respect of the production and use of some of the new chromium and cobalt complex dyestuffs, but the invention is not restricted to these Examples. The parts and percentages, unless otherwise stated, are parts and percentages by weight.

EXAMPLE 1

188 parts of 1-amino-2-hydroxybenzene-5-sulphonic acid amide are diazotised in known manner with a mixture of 150 parts by volume of 10-normal hydrochloric acid and a solution of 69 parts of sodium nitrite in 200 parts of water. The resultant solution of the diazonium salt is poured at 5° C. into a saturated aqueous solution of 380 parts of crystallised sodium sulphite. The mixture is stirred for another hour at 5° C., the deposited diazosulphonate filtered off under reduced pressure and washed with dilute

aqueous sodium chloride solution. A suspension of the resultant diazosulphonate in 15,000 parts of water has added to it at about 20° C. 192 parts of sodium dithionite, the diazosulphonate thereby passing into solution and the solution losing its colour. 400 parts of concentrated hydrochloric acid and 147 parts of isatin are added to the said solution and heated for 3 hours at 90° to 100° C. The reaction product is filtered under reduced pressure and the residue washed until showing a neutral reaction. After drying at 70° C., 265 parts of the dyestuff of the formula



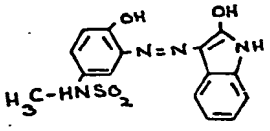
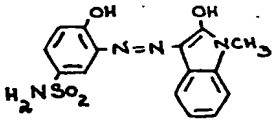
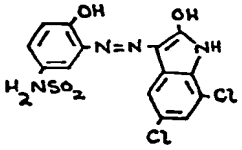
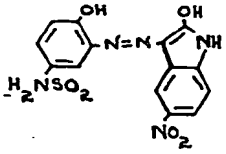
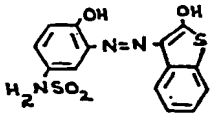
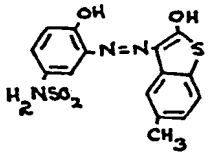
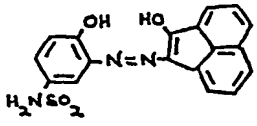
are obtained.

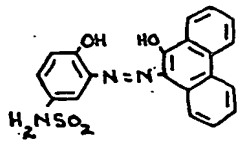
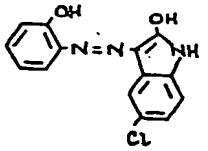
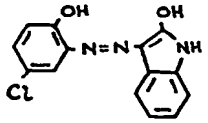
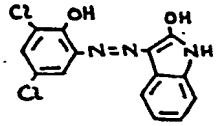
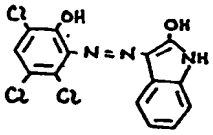
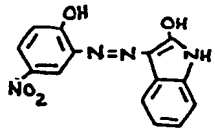
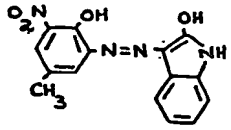
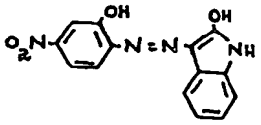
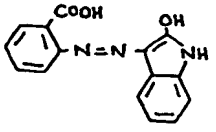
The same dyestuff is obtained by stirring the diazonium salt solution with a solution of 452 parts of crystallised tin (II) chloride in 800 parts of 10-normal hydrochloric acid for 30 minutes at 5° C., adding 147 parts of isatin, stirring for three hours at 90° C. to 100° C. and working up as described above.

332 parts of this dried azo dyestuff and 272 parts of crystallised sodium acetate are made into a paste with 3,000 parts of formamide and then a solution of 160 parts of crystallised chromium (III) chloride in 500 parts of formamide is added at 70° C. The mixture is stirred at 80° to 90° C. until the metal complex has been completely formed. Then the dyestuff solution is introduced into about 3,000 parts by volume of water and the dyestuff salted out. 350 parts of a dyestuff are obtained which dyes wool from a neutral bath brilliant red shades.

If the metal-free azo dyestuff is reacted with 237 parts of cobalt (II) chloride in water, instead of with chromium (III) chloride, there is obtained a dyestuff which dyes wool and polyamide fibres fast orange-brown shades.

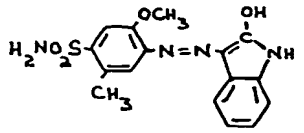
The following dyestuffs can be obtained in a corresponding manner:

Example No.	Dyestuff	Complex metal	Colour of dyeing on wool
2		chromium	red
3		chromium	red
4		chromium	red
5		chromium	red
6		chromium	red-violet
	" "	cobalt	red
7		chromium	red-violet
8		chromium	green
	" "	cobalt	olive-green

Example No.	Dyestuff	Complex metal	Colour of dyeing on wool
9		chromium	reddish-blue
	" "	cobalt	olive-green
10		chromium	bluish-red
11		chromium	bluish-red
12		chromium	bluish-red
13		chromium	yellowish-red
14		chromium	red
15		chromiun	Bordeaux
16		chromium	violet
	" "	cobalt	red-violet
17		chromium	greenish-yellow

EXAMPLE 18

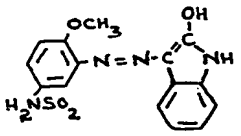
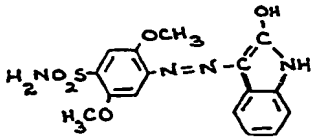
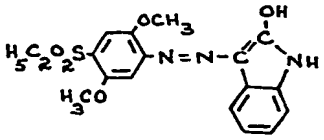
216 parts of 1 - amino - 2 - methoxy - 5 - methylbenzene - 4 - sulphonic acid amide in a solution of 250 parts by volume of 10-normal hydrochloric acid in 3,000 parts of water are diazotised with a solution of 69 parts of sodium nitrite in 200 parts of water at 5° C. At the same temperature, this diazo solution is poured rapidly into a saturated solution of 630 parts of crystallised sodium sulphite and the mixture stirred for half an hour. Then 250 parts by volume of 10-normal hydrochloric acid are allowed to flow in, 50 parts of acetic acid are added and the solution decoloured by strewing in zinc dust. The solution filtered from the zinc sludge is stirred with 1000 parts of concentrated hydrochloric acid and 147 parts of isatin for 3 hours at 90° to 100° C. The deposited dyestuff is filtered off under reduced pressure, washed and dried at 70° C. 320 parts of the azo dyestuff of the formula:



are obtained.

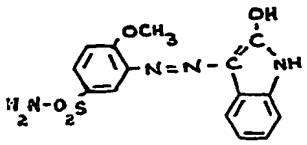
360 parts of the dried azo dyestuff are suspended in 3,000 parts of diglycol. To this solution there is gradually added a solution of 320 parts of crystallised chromium (III) chloride in 1000 parts of diglycol. The temperature of the mixture is raised to 120° to 130° C. and the mixture stirred until the metal complex has formed completely. The reaction mixture is introduced into 40,000 parts of water while stirring, the reaction product precipitated by the addition of sodium acetate, filtered under reduced pressure and dried.

Dyestuffs having similar properties are obtained by reacting the azo dyestuffs in the following Table in the same way with chromium (III) chloride:

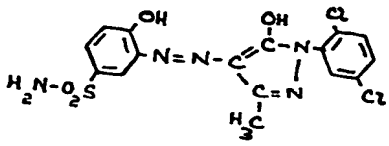
Example No.	Azo dyestuff	Shade of dyeing on wool
19		red
20		red-violet
21		red-violet

EXAMPLE 22

An aqueous suspension containing 0.05 mol of the 1:1-chromium complex compound of the dyestuff:



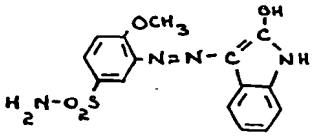
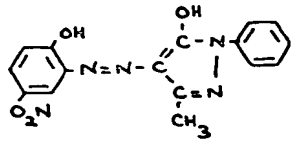
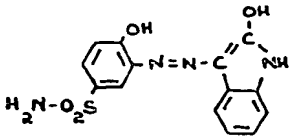
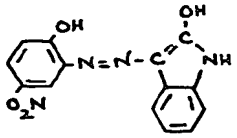
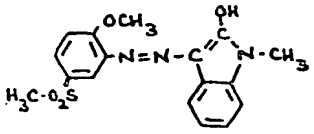
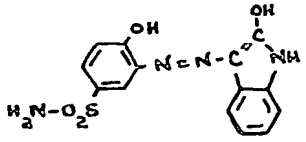
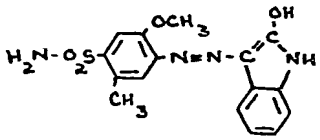
is dissolved in 800 parts of water by the addition of 8 parts of 50% sodium hydroxide solution and to the resultant solution there is added an aqueous paste which contains 0.05 mol of the dyestuff:



and the mixture is heated while stirring at 90° C. until the complex has completely formed. The end of the reaction has been achieved when a sample of the reaction mix-

ture is paper-chromatographically uniform. The mixture is allowed to cool and is neutralised with acetic acid. The dyestuff precipitated by adding aqueous sodium chloride solution is filtered under reduced pressure and dried. It dyes wool and polyamide fibres uniform yellowish red shades from a neutral or weak acid bath. The dyeings are very fast to light, fulling and washing.

Metal complex dyestuffs with similar properties are obtained in the same way from the dyestuffs in the following Table:

Example No.	1:1 chromium complex the azo dyestuff	Metal-free dyestuff	Shade of the dyeing on wool
23			yellowish-red
24			bluish-red
25			bluish-red
26		ditto	Bordeaux

EXAMPLE 27

100 parts of a woollen fabric are introduced at 45° C. into a bath which contains 3000 parts of water, 2 parts of the chromium complex dyestuff from Example 1, 2 parts of the sodium sulphonate of the reaction product of 80 mols of ethylene oxide and 1 mol of octadecyl alcohol, and 5 parts of ammonium acetate. The dyebath is heated to 98° C. within 45 minutes and then kept for another 15 minutes at this temperature.

A brilliant red dyeing with very good fastness properties is obtained.

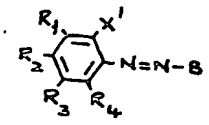
EXAMPLE 28

100 parts of a polycaprolactam textile are dyed for 30 minutes at the boiling temperature in a bath which contains 2000 parts of water, 1 part of the cobalt-containing dyestuff from Example 16, 4 parts of a 25% aqueous ammonia solution, 1 part of N,N-bis-(2-hydroxyethyl)-amine and 1 part of the reaction product of 30 mols of ethylene oxide and 1 mol of octadecyl alcohol. 4 parts of ammonium sulphate are then added and the dyebath allowed to boil for another 30 minutes.

A red-violet dyestuff of excellent fastness properties is obtained.

WHAT WE CLAIM IS:—

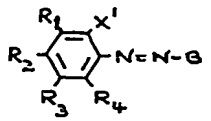
1. Any metal complex which contains, combined to one chromium or cobalt atom, one to two radicals of the general formula:



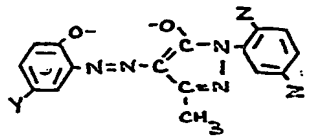
in which X^1 represents an oxygen atom or a —COO— group, R_1 represents a hydrogen atom, a chlorine atom or a nitro group, R_2 represents a hydrogen atom, a nitro group, a methylsulphone group, an ethylsulphone group or a sulphonic acid amide group, R_3 represents a hydrogen atom, a chlorine atom, a methyl group, a methoxy group, a nitro group, a methylsulphone group, an ethyl-

sulphone group, a sulphonic acid amide group and a sulphonic acid methylamide group, R_4 represents a hydrogen atom or a chlorine atom and B represents a 2-hydroxyindolyl-3, a 1 - methyl - 2 - hydroxyindolyl - 3, a 2 - hydroxy - 5 - chlorindolyl - 3, a 2 - hydroxy - 5,7 - dichloroindolyl - 3, a 2-hydroxy-5 - nitroindolyl - 3, a 2 - hydroxythionaphthyl - 3, a 2 - hydroxy - 5 - methylthionaphthyl-3, a 2 - hydroxy-acenaphthyl-1 or a 9-hydroxy-phenanthryl-10 radical.

2. Any metal complex which contains, combined to one chromium or cobalt atom, one radical of the general formula:

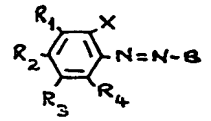


and another radical of the above formula or a radical of the formula:



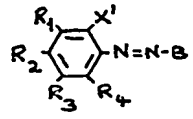
in which X^1 represents an oxygen atom or a —COO— group, R_1 represents a hydrogen atom, a chlorine atom or a nitro group, R_2 represents a hydrogen atom, a nitro group, a methylsulphone group, an ethylsulphone group, or a sulphonic acid amide group, R_3 represents a hydrogen atom, a chlorine atom, a methyl group, a methoxy group, a nitro group, a methylsulphone group, an ethylsulphone group, a sulphonic acid amide group or a sulphonic acid methylamide group, R_4 represents a hydrogen atom or a chlorine atom, B represents a 2-hydroxy-indolyl-3, a 1 - methyl - 2 - hydroxyindolyl - 3, a 2 - hydroxy - 5 - chlor - indolyl - 3, a 2 - hydroxy - 5,7 - dichlorindolyl - 3, a 2 - hydroxy - 5 - nitroindolyl - 3, a 2 - hydroxy - thionaphthyl - 3, a 2 - hydroxy - 5 - methyl - thionaphthyl - 3, a 2 - hydroxy - acenaphthyl - 1 or a 9 - hydroxy - phenanthryl - 10 radical, Y represents a sulphonic acid amide radical or a nitro group and Z represents a hydrogen atom or a chlorine atom.

3. A process for the production of chromium or cobalt complex dyestuffs wherein an agent supplying chromium or an agent supplying cobalt is allowed to act on an azo dyestuff of the general formula:

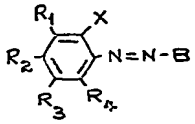


in which X represents a hydroxy group, a methoxy group or a carboxy group, R_1 represents a hydrogen atom, a chlorine atom or a nitro group, R_2 represents a hydrogen atom, a nitro group, methyl-sulphone group, an ethylsulphone group or a sulphonic acid amide group, R_3 represents a hydrogen atom, a chlorine atom, a methyl group, a methoxy group, a nitro group, a methylsulphone group, an ethylsulphone group, a sulphonic acid amide group or a sulphonic acid methylamide group, R_4 represents a hydrogen atom or a chlorine atom and B represents a 2-hydroxyindolyl-3, a 1 - methyl - 2 - hydroxyindolyl - 3, a 2 - hydroxy- 5 - chlorindolyl - 3, a 2 - hydroxy - 5,7 - dichlorindolyl - 3, a 2 - hydroxy - 5 - nitroindolyl-3, a 2 - hydroxy - thionaphthyl - 3, a 2-hydroxy - 5 - methyl - thionaphthyl - 3, a 2 - hydroxy - acenaphthyl - 1 or a 9-hydroxy - phenanthryl - 10 radical.

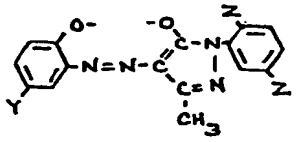
4. A process for the production of chromium or cobalt complex dyestuff wherein a complex dyestuff which contains, combined with one chromium or cobalt atom, a radical of the formula:



is reacted with an azo dyestuff of the formula:



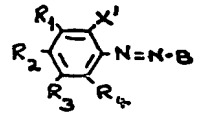
or an azo dyestuff of the formula:



in which X^1 represents an oxygen atom or a —COO— group, R_1 represents a hydrogen atom, a chlorine atom or a nitro group, R_2 represents a hydrogen atom, a nitro group, a methylsulphone group, an ethylsulphone group or a sulphonic acid amide group, R_3 represents a hydrogen atom, a chlorine atom, a methyl group, a methoxy group, a nitro group, a methylsulphone group, an ethylsulphone group, a sulphonic acid amide group or a sulphonic acid methylamide group, R_4 represents a hydrogen atom or a chlorine atom, B represents 2 - hydroxyindolyl-3, a 1 - methyl - 2 - hydroxyindolyl - 3, a 2-

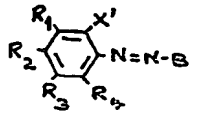
hydroxy - 5 - chlorindolyl - 3, a 2-hydroxy-5,7 - di - chlorindolyl - 3, a 2 - hydroxy-5 - nitroindolyl - 3, a 2 - hydroxy - thionaphthyl - 3, a 2 - hydroxy - 5 - methyl-thionaphthyl - 3, a 2 - hydroxy - acenaphthyl - 1 or a 9 - hydroxyphenanthryl-10 radical, X represents a hydroxy group, a methoxy group or a carboxy group, Y represents a sulphonic acid amide radical and a nitro group and Z represents a hydrogen atom or a chlorine atom.

5. A process for dyeing wool, synthetic linear polyamides and synthetic linear polyesters wherein a metal complex is used which contains, combined to a chromium or cobalt atom, one to two radicals of the general formula:

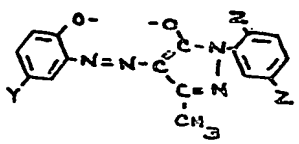


in which X^1 represents an oxygen atom or a —COO— group, R_1 represents a hydrogen atom, a chlorine atom or a nitro group, R_2 represents a hydrogen atom, a nitro group, a methylsulphone group, an ethylsulphone group or a sulphonic acid amide group R_3 represents a hydrogen atom, a chlorine atom, a methyl group, a methoxy group, a nitro group, a methylsulphone group, an ethylsulphone group, a sulphonic acid amide group or a sulphonic acid methylamide group, R_4 represents a hydrogen atom or a chlorine atom and B represents a 2-hydroxyindolyl-3, a 1 - methyl - 2 - hydroxyindolyl - 3, a 2 - hydroxy - 5 - chlorindolyl - 3, a 2 - hydroxy - 5,7 - dichlorindolyl - 3, a 2 - hydroxy - 5 - nitroindolyl-3, a 2-hydroxy-thionaphthyl - 3, a 2 - hydroxy - 5 - methyl-thionaphthyl-3, a 2-hydroxy-acenaphthyl-1 or a 9-hydroxy-phenanthryl-10 radical.

6. A process for dyeing wool, synthetic linear polyamides and synthetic linear polyesters wherein a metal complex is used which contains a chromium or cobalt atom to which is combined a radical of the general formula:

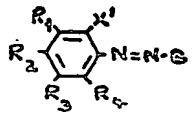


and another radical of the above formula or a radical of the formula:



in which X^1 represents an oxygen atom or a —COO— group, R_1 represents a hydrogen atom, a chlorine atom or a nitro group, R_2 represents a hydrogen atom, a nitro group, a methylsulphone group, an ethylsulphone group or a sulphonic acid amide group, R_3 represents a hydrogen atom, a chlorine atom, a methyl group, a methoxy group, a nitro group, a methylsulphone group, an ethylsulphone group, a sulphonic acid amide group or a sulphonic acid methylamide group, R_4 represents a hydrogen atom or a chlorine atom, B represents a 2 - hydroxyindolyl - 3, a 1 - methyl - 2 - hydroxyindolyl - 3, a 2 - hydroxy - 5 - chlorindolyl-3, a 2 - hydroxy - 5,7 - dichlorindolyl - 3, a 2 - hydroxy - 5 - nitroindolyl - 3, a 2-hydroxy - thionaphthyl - 3, a 2 - hydroxy-5 - methyl - thionaphthyl - 3, a 2 - hydroxy-acenaphthyl - 1 or a 9 - hydroxy - phenanthryl - 10 - radical, Y represents a sulphonic acid amide radical or a nitro group and Z represents a hydrogen atom or a chlorine atom.

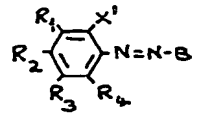
7. Textile materials of wool, synthetic linear polyamides, synthetic linear polyesters or mixtures of wool and synthetic linear polyesters, which have been dyed with a metal complex which contains, combined with one chromium or cobalt atom, one to two radicals of the general formula:



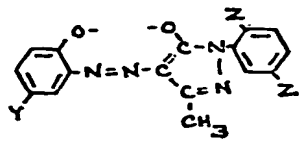
in which X^1 represents an oxygen atom or a —COO— group, R_1 represents a hydrogen atom, a chlorine atom or a nitro group, R_2 represents a hydrogen atom, a nitro group, a methylsulphone group, an ethylsulphone group and a sulphonic acid amide group, R_3 represents a hydrogen atom, a chlorine atom, a methyl group, a methoxy group, a nitro group, a methylsulphone group, an ethylsulphone group or a sulphonic acid methylamide group, R_4 represents a hydrogen atom or a chlorine atom and B represents a 2-hydroxyindolyl-3, a 1 - methyl - 2 - hydroxyindolyl - 3, a 2 - hydroxy - 5 - chlorindolyl - 3, a 2 - hydroxy - 5,7 - dichlorindolyl - 3, a 2 - hydroxy - 5 - nitroindolyl - 3, a 2 - hydroxy - thionaphthyl - 3, a 2 - hydroxy - 5 - methyl-thionaphthyl - 3, a 2 - hydroxy - acenaphthyl - 1 or a 9 - hydroxy - phenanthryl-10 radical.

8. Any textile material of wool, a synthetic linear polyamide, a synthetic linear polyester, or a mixture of wool and synthetic linear polyester which has been dyed with a metal complex which contains, combined with

a chromium or cobalt atom, a radical of the general formula:



and another radical of the above formula or a radical of the formula:



in which X^1 represents an oxygen atom or a —COO— group, R_1 represents a hydrogen atom, a chlorine atom or a nitro group, R_2 represents a hydrogen atom, a nitro group, a methylsulphone group, an ethylsulphone group or a sulphonic acid amide group, R_3 represents a hydrogen atom, a chlorine atom, a methyl group, a methoxy group, a nitro group, a methylsulphone group, an ethylsulphone group, a sulphonic acid amide group or a sulphonic acid methylamide group, R_4 represents a hydrogen atom or a chlorine atom, B represents a 2 - hydroxyindolyl - 3, a 1 - methyl - 2 - hydroxyindolyl - 3, a 2 - hydroxy - 5 - chlorindolyl - 3, a 2 - hydroxy - 5,7 - dichlorindolyl - 3, a 2 - hydroxy-5-nitroindolyl-3, a 2-hydroxy-thionaphthyl - 3, a 2 - hydroxy - 5 - methyl - thionaphthyl-3, a 2 - hydroxy-acenaphthyl-1 or a 9 - hydroxy-phenanthryl-10-radical, Y represents a sulphonic acid amide radical or a nitro group, and Z represents a hydrogen atom or a chlorine atom.

9. The process for the production of metal complex dyestuffs as claimed in claim 1 or 2 substantially as described in any of the foregoing Examples 1 to 26.

10. The dyeing process substantially as described in the foregoing Examples 27 or 28.

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